LIFETIME MODELING OF TiN ELECTRODES FOR AMTEC CELLS

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Abstract

In order to model the lifetime of the electrochemical cell in an Alkali Metal Thermal to Electric Converter (AMTEC). studies of TiN electrodes on β"-alumina solid electrolytes (BASE) have been made to determine the performance parameters over time. The first of a series of experiments in which TiN electrodes are studied in a Vapor Exposure Test Cell is described here, with preliminary results from electrochemical measurements made on the cell. The TiN electrodes tested here perform well. with minimal degradation over 1000 hours of operation at 850°C.

INTRODUCTION

AMTEC, the Alkali Metal Thermal to Electric Converter. is a direct energy conversion device capable of near-Carnot efficiencies; it has been demonstrated to perform at high power densities, with open circuit voltages in single electrochemical cells up to 1.6 V and current densities up to 2.0 A/cm^2 (Weber, 1974; Cole, 1983). As a power system, AMTEC is expected to deliver 20-25 W/kg. The work described in this paper is part of a study to determine the suitability of AMTEC power conversion in NASA's X2000 spacecraft program for exploration of the Solar System's outer planets.

An AMTEC converter must have a lifetime of S-7 years to provide power for a mission to Europa and 13-15 years to provide power for a mission to Pluto. Previous work on modeling the lifetime of AMTEC cells has focused on the electrode, as it is the component most likely to degrade with time. This work extends our previous work in electrode life modeling (Ryan et d., 1994) to include TiN electrodes, which are baselined as the electrodes to be used in AMTECs for spacecraft applications. Work on characterizing the electrode will also focus on other cell components such as the current collection network and the electrolyte; the work presented here focuses on the electrode and on the current collection network and electrolyte to the extent that they influence electrode performance.

Previously, several tests of 1000-3000 hours have been done to determine the nature of change in AMTEC components (Ryan et al., 1993, 1994). Components are heated in sodium atmosphere and operated at temperatures at or above the normal operating temperatures. Characterization of the physical and chemical changes in the components then makes it possible to determine acceleration factors as raised temperature. and accelerated testing can be init iated. There are restrict ions on the temperatures to which cell may be raised because the component with the lowest melting point, in the current design the metal-to-ceramic braze seal, will determine the maximum temperature at which the cell] may be operated To model overall lifetime, component tests which do not include the braze are operated at significantly' higher temperatures.

This work includes the preliminary analysis of electrochemical measurements made on TiN electrodes operated at 850oC over 950 hours in sodium atmosphere. Further analysis of the electrochemical measurements will be necessary for understanding of the operation of TiN electrodes. in addition, morphological and chemical analysis

of the electrodes and the electrolyte will be done to correlate electrochemical performance with morphological and chemical changes

The understanding developed in the experiment described here will be used to determine acceleration factors for accelerated operation of AMTEC components. Accelerated operation will allow prediction of the lifetime and possible failure mechanisms of AMTEC cells.

TiN ELECTRODE STUDIES

Titanium nitride electrodes have been extensively tested in AMTEC cells, and have shown relatively high power densities and performance (Asakami *et al.*, 1990 and Sievers *et al.*, 1993). A particular advantage of TiN electrodes has been presumed to be its stability against grain growth and material migration, and therefore its potential for use in long-lived devices. There are two types of TiN formulations used in state-of-the-art AMTECs. Sputtered TiN electrodes are used on the low pressure side of BASE as cathodes, and Weber process electrodes are used on the high pressure side as anodes. The two different types were tested together in a Vapor Exposure Test Cell (VETC) so their performance and grain growth characteristics could be compared directly.

The VETC is a testing apparatus which allows the operation of electrode materials as two electrode cells in alkali metal atmosphere. It is not a power producing cell, as the electrodes are held in the same pressure of sodium vapor. Electrodes are deposited on BASE and contacted as they would be in an AMTEC cell, but are operated as electrochemical cells, generally potentiostatically. These cells are not power-producing, but potentiostatic operation allows extraction of electrode and electrolyte performance parameters from current vs. voltage measurements and from Electrochemical Impedance Spectroscopy (EIS). It is a relatively simple setup which allows electrode testing without mounting an entire AMTEC experiment, and has been described in detail elsewhere (Ryan *et al.*, 1993).

EXPERIMENTAL

Two samples of TiN deposited on BASE were provided by AMPS, Inc. One type of TiN was 1 μm thick, made by reactive sputtering of titanium in a nitrogen atmosphere. The other type is a 20 μm thick TiN electrode applied to the electrolyte as a slurry and fired after application; this material is commonly known as a Weber process electrode. Both TiN electrode types were contacted with molybdenum screens tied on with molybdenum wire, and mounted on an a-alumina support inside a titanium tube, Molybdenum leads were attached to the Mo screens, and brought to the outside of the containment. Thermocouples were attached to the BASE tubes to record temperature over the life of the experiment. The titanium tube was placed in a stainless steel tube and sealed, The assembly was evacuated and baked at 300°C. When the pressure held at < 1x10^{-4} Pa. 10 g of sodium were introduced to the cell and held in a pool at the cold end of the stainless steel tube, The sodium was kept at a temperature which would provide sodium pressure similar to that on the low pressure side of an AMTEC cell. The temperature was controlled from 200 - 400°C with heating tapes.

The assembly was heated to 850°C over a period of several days. During the heating process, EIS data were taken. and will be used in the future to analyze BASE ionic conductivity as a function of temperature. When the electrode - electrolyte assembly reached 850°C, heating was stopped. The cell was held at temperature for 950 hours. and iV cur-w and EIS were recorded daily. Sodium temperature was varied between 200 and 400°C in order to gain understanding of the electrochemical processes influencing electrode performance.

RESULTS AND DISCUSSION

Electrode performance parameters which can be derived from the electrochemical data taken include R_{ser}, the series resistance of the leads, current collector, electrode and electrolyte; R_{con}, the contact resistance between the current collector and the electrode; R_{act}, *the* apparent charge transfix resistance at the electrode (sodium oxidation and reduction); B, the temperature independent exchange current at the electrode - electrolyte interface, and; G, the electrode morphology factor. These parameters have been described and the derivation discussed in detail elsewhere (Williams, *et al.*, 1990).

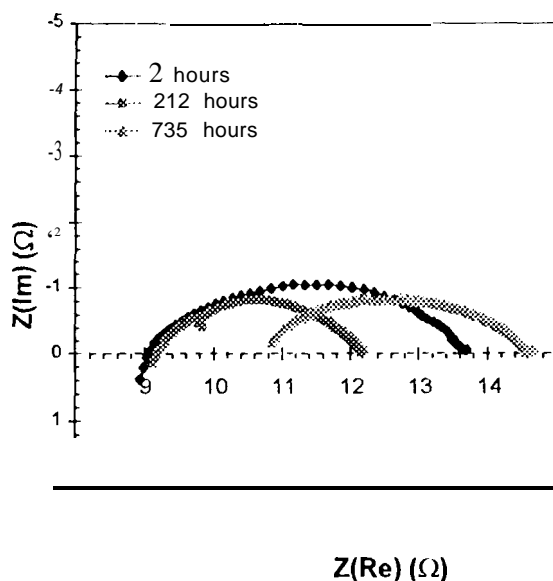## Sputtered Electrodes

Z(Re) (Ω)

FIGURE 1. Complex Plane EIS Plots of Sputtered Electrodes

Figure 1 shows an example of EIS complex plane (Nyquist) plots of the impedance measurements between two sputtered electrodes, taken after 2, 212, and 735 hours at 850°C in sodium atmosphere. Sodium temperature at these measurements was ~280°C, which corresponds to a pressure of -2 Pa. The series resistance, R_{ser}, can be taken from the low frequency intercept of the imaginary component of the impedance $(Z(Im))$ with the real axis $(Z(Re))$. This represents the resistances in both elect rodes. Over a period of 735 hours, R_{ser} increased from 9 to 10.8 Ω.

The apparent charge transfer resistance, R_{act}, *is* the difference between the low frequency and high frequency intercepts of $Z(Im)$ with the real axis, $Z(Re)$. R_{act} represents primarily the resistance to sodium oxidation and sodium ion reduction in the electrochemical cell. Over the first 210 hours, R_{act} decreased from 4.5 Ω to 3.1Ω, then increased slightly during the next 500 hours to 3.4 Ω. The initial decrease in R_{act} is consistent with electrode maturation, as has been found in several other electrodes (Ryan, et *al.*, 1991); the slow increase after maturation is also consistent with behavior found in other electrodes. Further analysis of R_{act} data, and examination of the time dependence of the change will allow prediction of the rate at which R_{act} will increase with time.

Figure 2 shows iV curves taken on the same electrode pair and under conditions similar to the conditions of the EIS data discussed above. These curves show very little limiting current as potential increases. The high potential region of the iV curve is the transport region, and analysis of these curves allows calculation of G, the morphology factor. As the limiting current is difficult to determine from these curves, one can draw the conclusion that transport in these electrodes is very good. Previous experiments with TiN electrodes have shown G in the region of 50 - 100. Figure 3 shows an iV curve taken at 590 hours at higher sodium pressure (10 Pa); the curvature of the iV behavior makes it possible to extrapolate a limiting current; the Gs calculated from the higher pressure sodium iV curves are about 50; however, an extrapolated curve does not always give a reliable figure. Further analysis of the iV behavior using, fitting routines will be necessary to calculate a more reliable G.
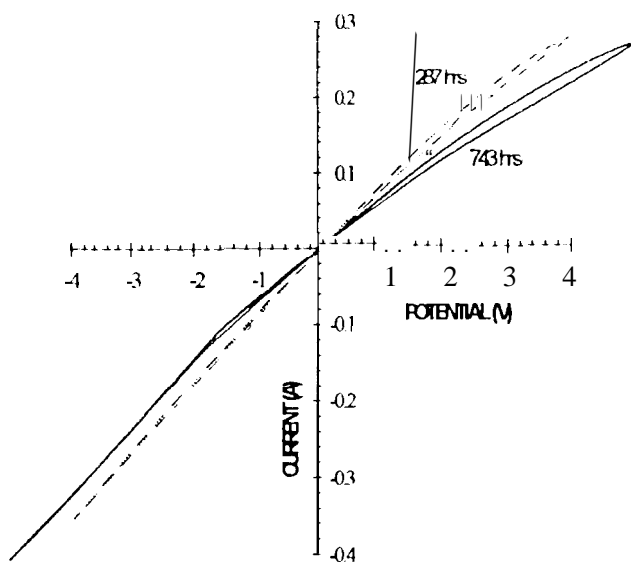
FIGURE 2. Current vs. Voltage Curves of Sputtered TiN Electrodes Operated at 850°C in 2 Pa Sodium Pressure.
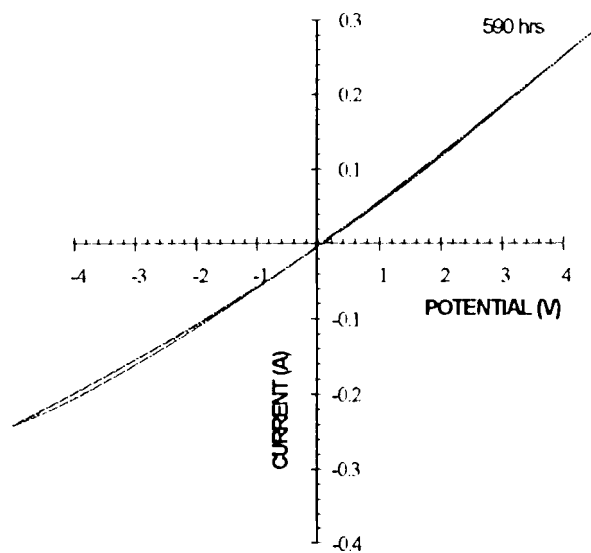
FIGURE 3. Current vs. Voltage Curve of Sputtered TiN Electrode Operated at 850°C in 8 Pa Sodium Pressure.

The exchange current may also be derived from iV curves by calculating it from the slope of the curve at the origin, Under AMTEC conditions, a temperature independent exchange current, B, has been defined; this value has not yet been computed for these electrodes. At present, comparison of the slope of the iV curve at similar conditions over time is a guide to changes in the exchange current, although other factors, such as transport impedance will influence the slope. As can be seen in Figure 2, the slope of the iV curve through the origin decreases slightly over time, indicating decrease in the exchange current. However, a comparison of the slopes under similar conditions over 750 hours shows 10°/0 decrease in the first 300 hours, followed by unchanged values for the following 600 hours.

Weber Electrodes

Weber process electrodes were studied in the same experiment using the same electrochemical techniques used on sputtered electrodes. As was found with sputtered electrodes, Weber process TiN electrodes are very good performance electrodes with good transport behavior. These electrodes are 20 pm thick, and show surprisingly good transport for such a thick material. Figure 4 shows EIS Nyquist plots of two Weber electrodes operated under the same conditions as the sputtered electrodes described above, 850°C at the electrodes and a sodium pressure of 2 Pa.

R_{act} in these electrodes is 0,8 Ω in the beginning of the experiment to and increases to 2.6 Ω at 735 hours. This value is significant}' smaller than the corresponding value in sputtered electrodes. The thickness of the Weber electrode, 20 μm, makes this small R_{act} somewhat surprising, as sodium transport in the electrode is not expected to be as good in a thick electrode as in a thin one, However, examination of the electrode before mounting the experiment showed several cracks in the TiN. which may serve as large

pores for sodium transport, while. the thickness of the TiN maintains good electrical contact for low resistance to electron transport

R_{scr} in these elect rodes is smaller than that in sputtered electrodes, going from 6.2 Ω in the beginning of the experiment to 7.2 Ω at 735 hours. This value for R_{scr} is not surprising, as the electrode is 20 μm thick and so sheet resistance in the electrode as well as contact resistance between the Mo screen and the electrode will be diminished compared with those resistances in the 1 μm thick sputtered electrode.

iV curves in Weber electrodes, shown in Figure 5 cou ld not be analyzed for G, as limiting cu rents were not reached. The curve at 287 hours is done in lower pressure sodium (2 Pa), while the 640 hour curve is done in 8 Pa sodium. Nevertheless, it was not possible to extrapolate a limiting current at either sodium pressure. Low G values indicated by this shape of the iV curve arc consistent with the low R_{act} and the possibility of cracks in the electrode contributing to good sodium transport.
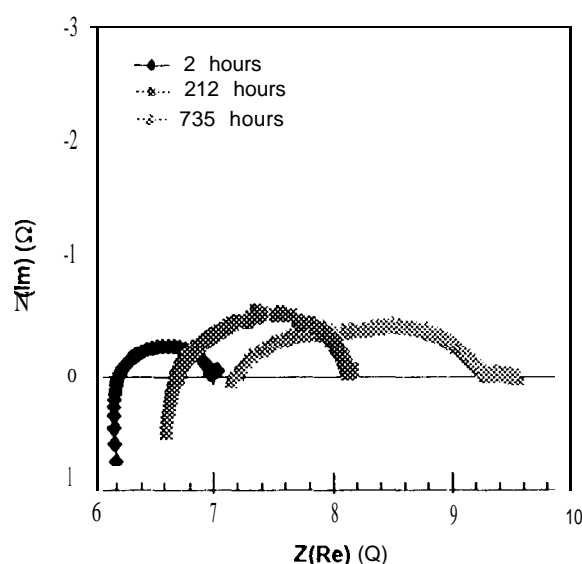
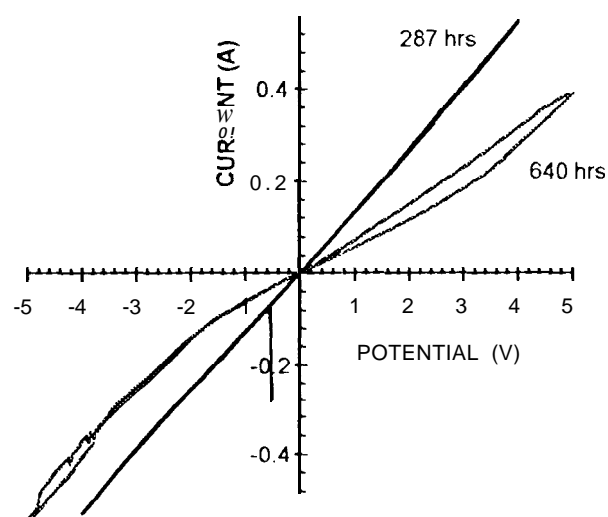FIGURE 4. Complex Plane EIS Plots of Weber Electrodes.

FIGURE 5. iV Curves of Weber Electrodes with 2 Pa (287 hrs.) and 8 Pa Sodium Pressure.

The slopes of the iV curves at the origin, and thus the exchange current, show a somewhat different pattern than that in the sputtered electrodes. There is the same initial drop of some 10% in the first 300 hours, but rather than leveling off for the remaining 600 hours, the slopes in Weber electrodes continue to drop. although at a somewhat diminished rate. This drop is consistent with the increasing R_{act} in Weber electrodes, in contrast to the much slower rate of increase in R_{act} in sputtered electrodes. The hysteresis in the 640 hour curve in Figure 5 indicates that there arc reactions in the electrode. As the slurry deposited TiN may contain other materials besides titanium and nitrogen, it is not unlikely that there arc several reactions taking place during operat ion, Post-experiment elemental analysis of the elect rode may elucidate some of these processes.

CONCLUSIONS

Preliminary analysis of electrochemical data on sputtered and Weber process TiN electrodes show them to be very good electrodes for both the anode and the cathode in AMTEC cells. They show only 10% degradation in slope at the origin in iV curves, which corresponds to similar decline in exchange current, and they show sodium transport behavior consistent with Gs of - 50. Weber electrodes appear to degrade longer than sputtered electrodes, but the rate may decrease with times longer than 1000 hours, as the 20 μm thick electrode will necessarily take much longer than the 1 μm thick sputtered electrode to matu re under AMTEC operating conditions.

Further analysis of the electrochemical data taken in this experiment, and correlation of those analyses with chemical and morphological analyses will be used to determine conditions for accelerated testing to elucidate and evaluate the reactions occurring at the electrode, the electrode-electrolyte interface, and the electrode-current collector interface. Accelerated testing of components and single-tube AMTEC cells will be used to model the lifetime and degradation mechanisms of AMTEC cells.

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